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## (54) RECOVERY OF COPPER

(71) We, THE ANACONDA COMPANY, a corporation organised and existing under the laws of the State of Montana, United States of America, of 25 Broadway, New York, State of New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to the recovery of copper from sulfide minerals or concentrates.

Ammoniacal leaching of copper ores and concentrates has a long history. Leaching of native copper and of oxidized copper ores (e.g. copper oxides, copper carbonates, copper silicates) presents no substantial difficulty for such materials react readily with ammoniacal leaching reagents when the leaching operation is carried out with free access to air. Ammoniacal leaching procedures have been employed since at least the early part of the twentieth century to recover copper from native and oxidized copper ores.

Copper sulfide minerals are also known to be soluble in ammoniacal solutions under oxidizing conditions. However, they are not as readily soluble as the oxidized minerals or native copper, and there are substantial differences in the ease with which different common sulfide copper minerals will dissolve. For example, chalcocite ( $\text{Cu}_2\text{S}$ ) dissolves with least difficulty, whereas chalcopyrite ( $\text{CuFeS}_2$ ) and enargite ( $\text{Cu}_3\text{AsS}_4$ ) dissolves only with considerable difficulty. Proposals to recover copper from sulfide minerals by ammoniacal leaching go back as far as the late nineteenth century. For example, U.S. Patent No. 581,160 proposes to extract copper from copper sulfides by leaching with a solution of aqueous ammonia and a nitrate such as ammonium nitrate. None of these early procedures for direct leaching of copper sulfides ever proved practical, however, and most of the early workers in ammoniacal leaching turned to roasting the sulfides in air and then leaching the oxidized copper from the roasted pro-

duct, as described for example in U.S. Patents No. 585,355 and 883,961. Such procedures, did not compete economically with conventional smelting techniques and had no advantages otherwise to recommend them, and so found no practical utilization.

A few decades ago interest developed in a procedure for extracting nickel from its sulfide ores by treatment with an ammoniacal solution under oxidizing conditions at high temperature and pressure. Copper is frequently associated with nickel in such ores and the procedure was applied to the recovery of copper as well. Such procedure, as described for example in U.S. Patents Nos. 2,576,314, 2,726,934 and 2,822,263, involves preparing a slurry of the ground mineral in an aqueous ammonia solution and heating such slurry with active agitation in an autoclave for a period of several hours. Air and ammonia are fed into the autoclave to supply the needs of the leaching reactions. Although the patents refer to conducting such a leaching operation at atmospheric pressure and at a temperature as low as  $100^\circ\text{F}$ ., they recognize that under such conditions leaching proceeds much too slowly to be of commercial interest. Accordingly, they describe procedures involving temperatures approaching or above the boiling point (typically  $175^\circ\text{F}$ . to  $225^\circ\text{F}$ .) and pressures of 30 to 100 psi. Even under these conditions, the procedures of these three patents have not been successful in leaching the difficultly soluble copper sulfides such as chalcopyrite and enargite.

The procedures of these three patents are the only ammoniacal leaching procedures that have ever been found suitable for commercial use in the extraction of copper from its sulfide minerals. Such use, however, has been limited to treatment of copper-bearing nickel ores, and the high value of the nickel recovered has doubtless been necessary to support the relatively costly autoclaving operation. No successful commercial use of the process in the treatment of conventional copper ores or concentrates, in which copper is the primary or sole metal value, is known.

This invention provides an improved process for leaching sulfide copper minerals with an ammoniacal solution to recover their copper content, using leaching vessels which operate at atmospheric pressure or so near atmospheric pressure (not exceeding 10 psig. and preferably below 8 psig.) that all the difficulties and expenses of high pressure or autoclave operations are avoided. The process of the invention provides for obtaining high recoveries (up to 99%) from copper concentrates that contain substantial proportions of such very difficultly soluble minerals as chalcopryite and enargite. Moreover, the process of the invention operates at temperatures low enough to be generated and maintained for the most part autogenously by the exothermicity of the leaching reactions. The new leaching process avoids generation of sulphur oxides or other atmospheric pollutants from the copper sulfide minerals themselves, and it leaves untouched in readily disposable solid form the substantial amount of iron sulfides (pyrites and pyrrhotite) which almost invariably are present in sulfide copperd ores and concentrates. The ammoniacal copper-bearing leach solution produced by the new process is readily treated to obtain metallic copper in marketable form, to regenerate the ammoniacal leach reagent, and to reject in solid, readily-disposable form the sulfur content of the copper minerals themselves.

Accordingly, this invention provides the method of recovering copper from sulfide copper minerals thereof which comprises forming a slurry of said minerals in finely divided form in an aqueous solution containing ammonium sulfate and free ammonia (present as ammonium hydroxide), passing said slurry at a pressure below that requiring autoclave equipment into a closed leaching vessel, maintaining the temperature of the slurry in the range from 50°C to 80°C whilst recirculating oxygen bearing gas from above the body of agitated slurry into that body at a substantial depth below the surface thereof, and withdrawing from said vessel slurry containing copper complexed with ammonia dissolved in the aqueous phase and mineral matter depleted in copper in the solid phase, characterized in that the body of slurry in said vessel is agitated with a vigour input of at least 0.05 horsepower per cubic foot of slurry in the vessel while introducing oxygen into the agitated slurry at a substantial depth below the surface of said body.

It is desirable that the leaching operation be conducted by passing the slurry sequentially through a series of leaching vessels.

The sulfide copper minerals may comprise copper ore or concentrates. Any other naturally occurring, or waste or intermediate, product containing copper in the form of a

sulfide with or without metallic copper e.g. cement copper also present (since metallic copper will also dissolve under the leaching conditions used in the method of the invention, it may be present in admixture with the sulfides). Products which lend themselves especially well to treatment by the new process are conventional copper flotation concentrates, which generally contain chalcocite and frequently also chalcopryite and other copper minerals.

Processes for leaching any nickel or zinc which may be in association with the copper are disclosed and claimed in our co-pending Applications Nos. 14421/73 and 13099/73 (Serial Nos. 1,404,246 and 1,404,245).

It is not essential that ammonium sulfate be present in the slurry as made up for introduction into the first leaching vessel, since ammonium sulfate is formed by oxidation of the sulfide copper minerals during the leaching operation. Moreover, regenerated ammoniacal solution produced from the leach liquor product will generally contain at least some ammonium sulfate, so as a practical matter, if the regenerated solution is recycled, it is present in the solution throughout the process.

The pH of the aqueous phase of the slurry is preferably maintained in the range from 9 to 11 throughout the leaching operation, in order to ensure the presence of free ammonia in optimum concentration for efficient conduct of the leach reactions. This may be done by adding free ammonia (preferably as gaseous ammonia) to the slurry in at least the first leaching vessel, where ammonia is preferably added at a rate corresponding substantially to the rate of the consumption. The concentration of free ammonia in each leaching vessel preferably is correlated with the temperature of the slurry in such vessel to maintain the pH of the slurry at such a value between 9 and 11 that the sum of the partial pressures of ammonia and water vapor over the slurry is considerably below the total pressure in the vessel. It is of course necessary for the total pressure to exceed the sum of the ammonia and water vapor partial pressures to allow for the admission of oxygen to the system, and it is desirable for the oxygen partial pressure to be at least 5 or 6 psi.

While air may be used to supply oxygen to the system, it is preferable to use commercial oxygen. The use of air involves adding a considerable partial pressure of nitrogen to the total pressure of the system; and since it is a major feature of the invention to operate at or near atmospheric pressure, it is best to add substantially pure oxygen and to avoid the continual addition of nitrogen which would accompany the addition of air.

The more readily soluble copper sulfides

dissolve first, in the first one or first few of the series of leaching vessels. These materials can be leached at the lower temperatures in the range from 50°C. to 80°C., and the reaction is favored by increasing the availability of free ammonia. Hence in the first leaching vessel, where the slurry temperature is lowest, ammonia may be added at a rate sufficient to establish a pH of about 10 or more. However, the pH preferably does not exceed 11 for the  $\text{Cu}(\text{OH})_2$  becomes a more stable copper product and inhibits the formation of the soluble ammonia complex. In the last leaching vessel of the series, where only the more difficultly dissolved copper sulfides are still in the solid phase, and where the temperature should be in the upper portion of the range to favor dissolution of these sulfides, the pH of the slurry is advantageously reduced to about 9.5 to ensure an adequate oxygen partial pressure.

The process of the invention can be carried out at atmospheric pressure. However, closed leaching vessels are necessary to avoid loss of free ammonia and otherwise to control conduct of the operation. Moreover, at the higher temperatures in the range necessary for reasonably rapid progress of the leaching reaction (50° to 80°C.) and at the preferred pH values in the range from 9 to 11, the sum of ammonia and water vapor partial pressures approaches closely to atmospheric. It is therefor advantageous to operate the leaching vessels under a slight positive pressure, not exceeding 10 psig. and preferably from 3 to 8 psig. At these low pressures the equipment used (leaching vessels, gas seals for closed systems, shaft packings, etc.) may be designed for atmospheric pressure, and the more costly equipment required for autoclave operation is not required.

As noted, the more easily dissolved minerals may be leached at lower temperatures and it is the more difficultly soluble minerals that persist undissolved in the solid phase to the latter leaching vessels in the series. It is advantageous, in treating copper concentrates generally, to maintain the temperature of the slurry in the first leaching vessel of the series in the range from 50° to 65°C., and to increase the slurry temperature by an amount of from 3 to 10°C. and preferably by substantially 5°C. in each subsequent vessel of the series. In the case of concentrates in which mainly chalcocite is present, but with a small proportion of none of the more difficultly soluble copper sulfides, the slurry temperature in the first leaching vessel is preferably maintained in the range from 50°C. to 60°C., and is discharged from the last vessel in the series at a temperature in the range from 65°C. to 75°C. But if the con-

centrates being treated comprise a substantial proportion of such difficultly soluble minerals as chalcopyrite and enargite, the temperature of the slurry in the first leaching vessel may be maintained in the range from 60°C. to 70°C., and the slurry in the last vessel in the series is preferably at a temperature in the range from 70°C. to 80°C.

The leaching reactions are exothermic and release ample heat to bring the temperature of the leach solution to the desired value and maintain it there, especially in the first leaching vessel of the series where most of the copper is dissolved. Indeed, it is necessary in many cases to provide for cooling the slurry in the first one or more leaching vessels to hold its temperature to the desired value. This can be done, of course, by providing cooling coils in the vessels, or surrounding them with a cooling jacket. In the last vessel of the series, or the last few of them, where most of the copper has been extracted from the solids and only the more difficultly and slowly dissolving copper minerals remain, the heat released by the leaching reaction may be insufficient to develop and maintain the relatively higher temperatures to which the slurry in these vessels should be heated. Hence here it may be necessary to supply heat to the slurry, by providing heating coils in the vessels or heating jackets around them.

The slurry in each leaching vessel is vigorously agitated throughout the conduct of the leaching operation. This advantageously is done by a motor driven impeller extending through the closed top of each leaching vessel. The vigor of slurry agitation should be great — at least 0.05 horsepower and preferably 0.1 horsepower or more input to the impeller per cubic foot of slurry in the vessel. This corresponds substantially to the vigor of agitation of the pulp in a froth flotation cell. With less vigorous agitation, the efficiency and rate of copper dissolution from the concentrates or other solids is undesirably reduced.

Simultaneously with such vigorous agitation of the slurry, there is vigorous recirculation of the oxygen-bearing gas from over the slurry in each vessel to a point well below its surface. This is best done by providing an external circulation system including a pump or blower for continuously withdrawing gas from the upper portion of the vessel interior and delivering it back into the vessel at a point near the bottom of the body of slurry. In small leaching vessels (less than six feet of slurry depth) it is possible to use a sub-aeration flotation impeller both to agitate the slurry and to recirculate the gas phase through the slurry. However, economical operation calls for larger leaching vessels in which the slurry may stand ten

or twelve feet deep, and in such vessels it is necessary for the gas recirculation to be independent of slurry agitation.

The time required for the leaching operation is generally in the range from 3 to 6 hours, 5 hours being typical. This in effect is the transit time for the slurry through the entire series of leaching vessels. It is generally possible in such a length of time to extract into the aqueous phase about 90% or more of the copper content of a typical copper concentrate containing largely chalcocite as the copper mineral but with significant proportions of chalcopryrite and other relatively difficultly soluble copper minerals also present.

The aqueous phase of the slurry withdrawn from the last leaching vessel in the series contains the dissolved copper in the form of a copper ammonium complex, and it contains the sulfur component of the dissolved copper minerals in the form of ammonium sulfate. It also contains residual free ammonia, and some small amounts of sulfamates and thionates. The solid phase, depleted in weight and bulk by the amount of the dissolved copper minerals, contains substantially all the remainder of the incoming material. For example, it contains unaltered the pyrites and pyrrhotite content of copper concentrates, and such earthy materials as silica and alumina. It will also contain any insoluble metal values such as silver and gold, and molybdenum sulfide.

The copper-rich aqueous phase is separated from the solid phase. The former then may be treated in any conventional manner to recover its copper content, to regenerate ammonium sulfate solution or free ammonia or both for reuse in the process, and for separating excess sulfate produced by oxidation involves re-slurrying the separated solids ponent of the minerals.

The solid phase, which may be separated from the liquid phase of the slurry at the conclusion of the leaching operation by any conventional procedure such as decantation thickening or filtration, may be discarded. However, it often will contain significant quantities of recoverable copper and the invention contemplates treating the separated solids by re-leaching in a secondary leaching operation. The secondary leaching operation particularly contemplated by the invention involves re-slurrying the separated solids in an aqueous ammonium sulfate solution containing free ammonia, and then treating them in a closed re-leaching vessel in a manner generally similar to that used in the primary leaching operation. The slurry, at a pressure not exceeding 10 psig., is brought to a lower pH and to a higher temperature than that prevailing on the average in the series of leaching vessels used for the primary leaching operation, and is vigorously

agitated in the re-leaching vessel while admitting oxygen thereto and vigorously recirculating oxygen-bearing gas from above the body of slurry in said vessel into said body at a substantial depth below its surface. Thereafter the copper-bearing aqueous phase is separated from the copper-depleted solid phase. The former may be united with the aqueous phase from the primary leaching operation, and the latter may be discarded or may be further treated to recover its residual metal values such as silver, gold and molybdenum.

Since the solids treated in the re-leaching operation contain the more difficultly soluble components of the original feed material, the re-leaching operation ordinarily proceeds more slowly than the primary leaching operation. For example, the re-leaching or secondary leaching operation may continue for five to eight hours, typically six hours; but since the volume of solids is small relative to that fed into the primary leaching operation, very large equipment is not required to provide for such a long re-leach.

Ammonia gas is preferably fed into the re-leaching operation, as it is to the primary leaching operation, to maintain the pH of the aqueous phase of the slurry at an optimum value, typically 9.5 but more generally in the range from 9.3 to 9.7. Heat may have to be supplied to bring the slurry in the re-leaching vessel to the desired value, which generally is in the range from 70°C. to 80°C., say 75°C. in a typical case.

Re-leaching may often be carried out in a single vessel; but it may also be conducted in a series of vessels through which the slurry flows sequentially. In the latter case it is desirable, as in the primary leaching operation, to maintain the temperature of the slurry higher and its pH lower in the second vessel of the series than in the first. For example, it may be 2° to 5°C. warmer, and have a pH of say 9.4 in the second vessel than the pH of 9.5 or 9.6 in the first vessel.

The re-leaching operation will in most cases serve to recover 90% or so of the copper present in the solids discharged from the primary leach. Thus overall a copper recovery of 99% or thereabouts is obtained from the original concentrates or other starting material.

The single figure of the accompanying drawing is a flow-sheet of an advantageous embodiment of the invention diagrammatically portraying apparatus that may be used for carrying out the process.

In the process of the flowsheet finely divided copper concentrates are formed into a slurry with an aqueous ammonia-ammonium sulfate solution in a closed slurry preparation vessel 10. The slurry then flows by gravity or is pumped to the first

of a series of primary leaching vessels 11, 12, 13, 14, and 15. The slurry is maintained to a depth indicated by the surface level L in each of the leaching vessels and flows by gravity sequentially through the series. Each of the closed vessels 11—15 may be provided with internal coils or a jacket (not shown) for circulating heating or cooling medium in heat-exchange relation with the slurry therein. Each vessel is provided with an agitator impeller 16 driven by a motor M for vigorously agitating the slurry. Each vessel also is equipped with a gas recirculating gas from above the surface level L of the slurry to a point deep below such surface level.

All this equipment, including seals for the impeller shafts, is constructed for operation at substantially atmospheric pressure. No special high-pressure autoclave construction or design is needed. It is sufficient that the slurry containing equipment be enclosed to confine the ammonia, oxygen and water vapor.

Oxygen is supplied to each of the leaching vessels 11—15 from a supply tank 18. The oxygen is delivered at a low super atmospheric pressure, for example 6 psig., through a pressure regulating valve P, and it maintains such pressure in each leaching vessel. Gaseous ammonia is supplied to each of the first two vessels 11 and 12 from a supply tank 19 through flowmeters F and valves V by which the rate of admission of the ammonia to each of these two vessels may be independently controlled.

Slurry is discharged from the last leaching vessel 15 in the series into a storage or holding tank 20 equipped with an agitation impeller 21 driven by a motor M. From the tank 20 the slurry flows into a thickener 22 from which the liquid phase containing dissolved copper overflows and from which the solids are collected in the form of a thickened mud underflow. The overflow solution is treated for copper recovery and to regenerate aqueous ammonia-ammonium sulfate solution which is recycled to the slurry make-up tank 10 for preparing additional slurry for leaching. A bleed side stream is taken from the regenerated solution to separate excess sulfate dissolved from the copper sulfide concentrates, and the ammonia recovered thereby is returned to the stream recycling to the slurry make-up tank (or it may be passed to ammonia storage).

The underflow from the thickener 22 is re-slurried or mixed with recovered aqueous ammonia-ammonium sulfate solution and is introduced into a secondary leaching tank 23. This tank is in all essential respects the same as primary leaching tanks 11, 12. It is equipped with an agitation impeller 24, a pump or blower 25 for vigorously

recirculating gas from above the liquid surface level L of slurry in the vessel to deep below such surface, and connections for supplying oxygen from the tank 18 and ammonia from the tank 19 through a flowmeter F and valve V. Optionally a second secondary leaching tank 26, equipped similarly to the first such tank 23, may be provided to receive the slurry outflow from the first tank.

The slurry discharged from the secondary leach tank 23, or from the second such tank 26 if provided, is delivered into a storage or holding tank 27 equipped with a motor-driven impeller 28. From this holding tank the slurry flows into the first of a series of thickeners 29, 30 and 31 where it is subjected to countercurrent washing with water. The advanced wash water joins with the copper-bearing leach solution decanted as overflow from the first thickener 29, and this solution is fed with the slurry from the primary leaching operation into the thickener 22 from which the clarified copper-bearing solution product of the leaching process is taken. The final washed underflow product from the last thickener 31 in the washing series is substantially completely depleted in copper and is sent to treatment for recovery of such values as it may contain (e.g. silver, gold molybdenum sulfide), or is discarded.

*Example* — Following is an exemplary embodiment of the process according to the invention as carried out in the apparatus and with the sequence of steps described above and shown on the accompanying flowsheet.

Copper concentrates containing 30% by weight copper largely in the form of chalcocite but also in substantial proportion as other minerals including covellite, enargite and chalcopyrite, are slurried in the tank 10 with an aqueous solution of ammonium sulfate and ammonium hydroxide containing 87 grams per litre of ammonia (both free and combined) and substantially no dissolved copper. This slurry is mixed in the proportions of about 1250 gallons of solution to 2500 pounds of wet concentrates (containing 20% by weight water), forming a slurry containing about 15% solids by weight. This slurry is pumped continuously into the first of the primary leaching tanks 11 and it flows from tank to tank through the series by gravity.

Commercially pure oxygen is fed into the first (and each subsequent) tank at 6 psig. through the pressure regulating valve P, and thereby the pressure in the series of leaching tanks is established at that value. Gaseous ammonia is metered into each of the first two tanks 11 and 12 through the appropriate flow meters and valves at a rate sufficient to maintain the pH of the slurry

in these tanks at about 9.9 This calls for a flow of ammonia into each tank at the rate of about 5.3 standard cubic feet per minute.

5 The slurry in each of the first two tanks (and in each other tank as well) as vigorously agitated by the impellers 16. Each tank contains about 60 gallons of slurry, and the impeller of each tank absorbs about six  
10 horsepower, corresponding to agitation with a vigor of substantially 0.1 horsepower per cubic foot of slurry.

The oxygen-bearing gas overlying the slurry level L in each of the five leaching tanks is vigorously circulated by the pump 15 17 into the slurry at a point near the bottom of the tank. The rate of such recirculation diminishes from tank to tank in conformity with the slowing down of the dissolution  
20 reactions as the slurry solids become depleted in the more readily soluble copper minerals. The rate of such circulation, in standard cubic feet per minute, is approximately 22 in the first tank 11, 14 in the  
25 second tank 12, 7.3 in the third tank 13, 4.7 in the fourth tank 14, and 2.1 in the fifth tank 15.

In the first tank 11, where the rate of copper dissolution is maximum and where almost half of the total copper content of the concentrates dissolves, the temperature of the slurry is maintained at 55°C. This requires cooling of the slurry by circulation  
30 of cooling water through cooling coils disposed in the tank, because of the large amount of heat released by the exothermic dissolution reactions. In the second tank 12 the temperature of the slurry is raised to 60°C., and here also it is necessary to  
40 cool the slurry to maintain it at this temperature. In this tank approximately another 25% of the total copper content of the concentrates dissolves, with a corresponding large heat release which is more than enough  
45 to raise the slurry temperature to the desired value and hold it there.

No gaseous ammonia is added to the slurry in the third, fourth and fifth tanks 13, 14 and 15, and consequently the pH of the aqueous phase diminished as the  
50 slurry passes through these tanks and additional copper is dissolved. In the third tank 13 the pH of the solution falls to about 9.7 while the temperature is raised to 65°C. The reduction in pH here is  
55 important in view of the rise in temperature, in order to maintain the sum of the partial pressures of ammonia and water vapor well below the 6 psi. established by the oxygen supply system and to maintain ample oxygen  
60 in the tank for efficient progress of the leaching reactions. Here the rate of copper dissolution is reduced, however, because the remaining copper minerals in the solid phase  
65 are mostly of difficultly soluble species. As

a consequence the heat released is only about enough to establish and maintain the desired slurry temperature. No cooling of the slurry is necessary, but on the other hand no heat is required to hold it close  
70 to the desired 65°C. Approximately 10% of the copper content of the concentrate is dissolved in this tank.

In the fourth and fifth tanks 14 and 15 the pH of the aqueous phase of the slurry is about 9.6 and 9.5 respectively, and the temperature is held close to 70°C. in both tanks. The rate of copper dis-  
75 solution in these tanks is slow, and in both tanks the slurry may be heated by circulation of heating fluid through coils in the tanks to establish and maintain the desired slurry temperature.

The retention time of the slurry in each tank is about one hour, so that the duration of the primary leach is in total about five  
85 hours.

The aqueous phase of the slurry from the first tank contains about 22 g/l copper, that from the second tank contains about 35  
90 g/l copper, that from the third contains about 42 g/l copper, and that from the fourth contains about 46 g/l copper. The final slurry discharged into the tank 21 has in its aqueous phase about 50 g/l copper, about 130 g/l total ammonia (of which  
95 about 10 g/l is free ammonia), about 54 g/l ammonia complexed with copper, and about 150 g/l sulfate ion. The solid phase of this slurry amounts to only about 100 pounds out of each ton of dry concentrates  
100 charged into the system. It contains all the pyrites and gangue (silica, alumina, etc.) constituents of the concentrates, and all the undissolved metal values such as gold and silver and including about 10% of the  
105 original copper content, mostly in the form of the difficultly soluble minerals chalcopyrite and enargite.

The slurry collected in the tank 20 is decanted in the thickener 22 to separate the  
110 aqueous phase as a clarified solution which can be treated for recovery of its copper content in metallic form and for recovery of ammonium sulfate, ammonium hydroxide solution for recycling to prepare fresh slurry  
115 with incoming concentrates.

The thickened underflow of solids from the thickener 22 contains about 65% by weight solids. This slurry is diluted to 50%  
120 solids by fresh ammonium sulfate — ammonium hydroxide solution and is introduced into the secondary leach tank 23. Here it is vigorously agitated similarly to the slurry in the primary leaching tanks, and the pH of the aqueous phase is brought  
125 to and maintained at about 9.6 by the introduction of gaseous ammonia at the rate of about 0.7 standard cubic foot per minute. Concurrently a commercially pure oxygen 130



is introduced at about 6 psig. As in the primary leaching operation, the oxygen-bearing gas overlying the body of agitated slurry is vigorously recirculated to near its bottom. The slurry is heated to 85°C. by circulation of heating fluid through coils in the vessel.

The rate of flow of slurry through the secondary leaching tank 23 is slow so that the retention time therein is about six hours. The flow through this tank and into the agitated storage tank 27 is by gravity. Approximately 90% of the copper content of the solid phase of the slurry fed into the secondary leaching tank 23 is dissolved in this tank, yielding substantially 99% recovery of copper from the original concentrates in the combined primary and secondary leaching operation.

The slurry collected in the secondary leach storage tank 27 contains in its aqueous phase about 68 g/l copper and 150 g/l ammonium ion (ammonium sulfate plus ammonium hydroxide). It also contains about 160 g/l sulfate. The solid phase of the slurry is substantially completely depleted in copper, but contains recoverable silver and gold values.

The slurry is fed from the storage tank 27 into the series of countercurrent washing thickeners 29, 30, 31. The aqueous phase overflowing the first thickener is united with the slurry from the primary leaching operation in the thickener 22. The solids content of the slurry from the secondary leach is washed substantially free of copper and collected as a thickened mud containing only about one half the total weight of concentrates fed into the system and assaying only about 0.6% copper.

#### WHAT WE CLAIM IS:—

1. The method of recovering copper from sulfide minerals thereof which comprises forming a slurry of said minerals in finely divide form in an aqueous solution containing ammonium sulfate and free ammonia (present as ammonium hydroxide), passing said slurry at a pressure below that requiring autoclave equipment into a closed leaching vessel, maintaining the temperature of the slurry in the range from 50°C to 80°C whilst recirculating oxygen-bearing gas from above the body of agitated slurry into that body at a substantial depth below the surface thereof, and withdrawing from said vessel slurry containing copper complexed with ammonia dissolved in the aqueous phase and mineral matter depleted in copper in the solid phase, characterized in that the body of slurry in said vessel is agitated with a vigour input of at least 0.05 horsepower per cubic foot of slurry in the vessel while introducing oxygen into the agitated slurry at a substantial depth below the surface of said body.

2. A method of Claim 1 wherein the leaching operation is conducted by passing the slurry sequentially through a series of leaching vessels.

3. The method according to either of the preceding claims wherein the concentration of ammonia in the leaching vessel is correlated with the slurry temperature in such vessel to maintain the partial pressure of ammonia plus the partial pressure of water vapour in such vessel below the total pressure therein.

4. The method according to any of the preceding claims wherein the aqueous phase of the slurry is maintained at a pH in the range from 9 to 11 throughout the leaching operation.

5. The method according to any of the preceding claims wherein free ammonia is added to the slurry in at least the first of the leaching vessels at a rate corresponding substantially to the rate of its consumption.

6. The method according to any of the preceding claims wherein the pressure maintained in the leaching vessel is below 10 psig.

7. The method according to Claim 6, wherein the pressure maintained in the leaching vessel is in the range from 3 to 8 psig.

8. The method according to any of the preceding claims wherein the slurry in the or each leaching vessel is agitated with a vigor input of at least 0.1 horsepower per cubic foot of slurry in the vessel.

9. The method according to Claim 2 wherein the pH of the aqueous phase of the slurry is substantially 10 in the first leaching vessel where the leaching temperature is at a minimum and is decreased to substantially 9.5 in the last leaching vessel of the series where the leaching temperature is at a maximum.

10. The method according to any of Claims 2, 6 and 7, wherein the temperature of the slurry in the first leaching vessel in the series is maintained in the range from 50°C to 65°C and is increased by an amount from 3 to 10°C in subsequent vessels of the series.

11. The method according to Claim 10, wherein the temperature is increased by substantially 5°C in subsequent vessels of the series.

12. The method according to either of Claims 10 and 11 wherein the copper minerals are in the form of a flotation concentrate containing a high proportion of chalcocite, the temperature of the slurry in the first leaching vessel is maintained in the range from 50°C to 60°C, and the slurry is discharged from the last leaching vessel at a temperature in the range from 65°C to 75°C.

13. The method according to either of

- Claims 9 and 10 wherein the copper minerals are in the form of a flotation concentrate containing a substantial proportion of chalcopyrite, the temperature of the slurry in the first leaching vessel is maintained in the range from 60°C to 70°C, and the slurry is discharged from the last leaching vessel at a temperature in the range from 70°C to 80°C.
14. The method according to any of the preceding claims wherein the solids containing residual undissolved copper separated from the copper-bearing leach solution are mixed with aqueous ammonium sulfate solution containing free ammonia (present as ammonium hydroxide) and are subjected to a secondary leaching operation at a pressure not exceeding 10 psig, in a closed leaching vessel while vigorously agitating the slurry in said leaching vessel and while admitting oxygen thereto and vigorously recirculating oxygen-bearing gas from above the body of slurry in said vessel into said body at a substantial depth below its surface, and thereafter separating the copper-bearing aqueous phase from the copper-depleted solid phase.
15. The method according to Claim 14, wherein the secondary leaching operation is continued for a period of time longer than the duration of the primary leaching operation.
16. The method according to either of Claims 14 and 15 wherein the secondary leaching operation is conducted in a single vessel.
17. The method according to either of Claims 14 and 15 wherein the secondary leaching operation is conducted by passing the slurry sequentially through a series of two or more vessels in the first of which the pH of the slurry is higher and its temperature is lower than in the last vessel in the series.
18. The method according to any of Claims 14 to 17 wherein the temperature of the slurry during the secondary leach is in the range from 70°C to 80°C.
19. The method for recovering copper from sulfidic copper minerals substantially as hereinbefore described with reference to and as shown in the accompanying drawing.
20. Copper recovered by a process as claimed in any of the preceding claims.
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